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Evaluation of Monitoring Techniques for
Dioxins in Ambient Air

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ABSTRACT

Chlorinated dibenzo-p-dioxins (CDDs) and dibenzofurans (CDFs) in ambient air have not been widely investigated. A few measurements of 2,3,7,8-tetra chlorodibenzo-p-dioxin (2,3,7,8-4CDD) in ambient air using high volume air sampling with glass fibre filters and polyurethane foam (PUF) cartridges have been reported. However, no validated methodologies for sampling ambient air for the full range of CDDs/CDFs have been presented. Proper validation requires spiking studies of multiple CDD/CDF congener to determine breakthrough of both the glass fibre filter and the PUF cartridges, and recovery studies to determine extraction efficiencies.

The Ontario Ministry of the Environment ambient air sampler for CDDs/CDFs consists of a glass fibre filter followed by a single or dual PUF cartridges. Low and high-level CDD/CDF surrogate spiking studies have been performed to determine the sampling efficiency of this device. ¹³C-labelled standards were spiked separately onto the glass fibre filter and PUF cartridges to determine breakthrough.

Initial results from a 24 hour sampling with a glass fibre filter and a single PUF indicated good spike recoveries for both the PUF and filter and some breakthrough of the lower congener spikes from the filter to the PUF.

INTRODUCTION

Interest in the analysis of CDDs and CDFs has increased over the past few years due to the knowledge of the toxic nature of these compounds. The methodology for the sampling and analysis of CDDs and CDFs in samples such as drinking water, fish, soils, sediments, effluents and stack emissions has been well developed. However, the analysis of dioxins and furans in ambient air has not been widely investigated because of the need for very low detection limits (pg/m^3). Another factor in the slow development of ambient air methodology is the selection of suitable sampling apparatus. CDDs and CDFs can exist in ambient air in two forms: 1) adsorbed on particulate matter and 2) as vapour phase molecules. It is also known that the concentrations found in either form may not necessarily be related to one another. One must be able to sample either the particulate, the vapour phase or both, as desired.

A number of sampling devices have been developed for monitoring ambient CDDs and CDFs. Most incorporate a particulate filter and an adsorbent material to trap vapour phase molecules, in series, attached to a vacuum source. Smith et.al. used a glass fibre filter, followed by silica gel in a removable cartridge (1). Silica gel was chosen as an adsorbent because it is easily cleaned and easily handled. Smith was able to obtain detection limits of $0.003 \text{ pg}/\text{m}^3$ for 2,3,7,8-TCDD but did not look at the full range of dioxin and furan congeners.

One of the more widely used adsorbents in ambient air monitoring is the polyurethane foam (PUF) plug. PUF is the material used in the upholstery industry and is inexpensive and convenient to handle. The PUF plug has been used by the U.S. Environmental Protection Agency to monitor 2,3,7,8-TCDD levels in ambient air(2). A glass fibre filter and a PUF plug housed in a General Metal Works, Inc., Model PS-1 air sampler was used. In laboratory spiked samples, 95% recovery of 2,3,7,8-TCDD was obtained, indicating the validity of the method for field samples(2). PUF adsorbents have also been used to monitor other types of volatile organic compounds such as pesticides (3,4), polycyclic aromatic hydrocarbons (4) and polychlorinated biphenyls (4) at the ng/m^3 level.

The Ontario Ministry of the Environment, Laboratory Services Branch and Air Resources Branch, has been evaluating one monitoring technique for the determination of total dioxin and total furan congeners in ambient air. The Ministry used a modified Hi-volume sampler with a glass fibre filter and single or dual PUF cartridges. Spiking experiments were carried out using ^{13}C -labelled dioxin and furan standards. The filters and PUF cartridges were spiked with different labelled congeners. The samplers were set up and air was drawn through the filter and PUF for extended periods of time. At the end of the sampling period, the filters and PUF cartridges were spiked with an additional labelled congener, extracted, cleaned and analyzed by GC/MS. Locations of the labelled congeners and their levels indicated if breakthrough from the filter to the PUF cartridge or from the PUF cartridge occurred and also indicated extraction efficiencies. High and low level spiking experiments were carried out with both single and dual PUF cartridges.

The results of these experiments are aiding the Ministry to develop both a sampling and analytical protocol that will later be evaluated under field conditions. Further feasibility and precision experiments will be required before a protocol can be determined.

EXPERIMENTAL

Materials - Glass fibre filters were obtained from Pallflex Products Corp. (Putnam, Conn.). Polyurethane foam was purchased from a local upholstery manufacturer. Distilled-in-glass grade solvents were used (Caledon Laboratories, Georgetown, Ontario). ^{13}C -labelled dioxin and furan standards were obtained from Cambridge Laboratories (Cambridge, MA.).

Apparatus - A modified Hi-Volume sampler with a single glass fibre filter and single or dual PUF cartridges was used. The samplers were assembled and spiked in the laboratory. A range of ^{13}C -labelled dioxin and furan standards were spiked on the filters and cartridges. Both high level (1-long/congeners) and low level (300-500 pg/congener) spikes were performed. Sampling was carried out for 24 hours in the case of a single PUF cartridge and for 72 hours when 2 PUF cartridges in series were used. Temperature and flow-rate data were monitored during the test period. Field blanks samples were also taken.

The aluminum filter housing and cartridge housings were cleaned with distilled water and solvents prior to usage. The PUF cartridges were cleaned before sampling by Soxhlet extraction with toluene for 24 hours. The cartridges were rinsed with methylene chloride and proven clean. The PUF cartridges were stored in clean aluminum foil prior to use.

Analysis - After sampling, the filters and cartridges were stored in pre-cleaned aluminum foil in a refrigerator prior to extraction. The filters and cartridges were extracted separately by Soxhlet extraction, with toluene for 24 hours. Prior to extraction the samples were spiked with ^{13}C -6CDD as an internal standard to provide extraction efficiencies. The extracts were concentrated to approximately 5-10 mL using a rotary evaporator. The dioxin/furan containing fractions were subjected to a modified Dow cleanup using NaOH/Silica, H_2SO_4 /Silica, AgNO_3 /Silica and activated alumina adsorbents. The final fraction was taken to dryness under a gentle stream of nitrogen and submitted for GC/MS analysis.

The GC/MS analysis was carried out using a Finnigan 4000 GC/MS/DS (Sunnyvale, CA.) in the selected ion monitoring mode. All ^{13}C -labelled congeners used were monitored in both the filter and cartridge samples. Percentage recoveries and breakthroughs of the congeners from the filters and from the cartridges were calculated.

Results and Discussion

An initial high level spike experiment using a glass fibre filter and a single PUF cartridge was carried out December 23, 1986. The spike recoveries for the filters are shown in Table 1 and for the cartridges are shown in Table 2. The samples were spiked with labelled dioxins (^{13}C -5CDD and ^{13}C -7CDD on the filters and ^{13}C -4CDD and ^{13}C -8CDD on the PUF cartridges) and were collected for a 24 hour period. The average sampling volume was 1800 m³. The recovery of ^{13}C -5CDD on the PUF indicated that there was some breakthrough of the lower congener from the filter onto the PUF cartridge.

Good recoveries for the other spiked congeners on both the filters and cartridges were observed for the field samples. The low spike recovery for the field blank samples can be partially accounted for by the low recovery of the ^{13}C -6CDD internal standard. Good detection limits (0.02 pg/m^3 for 4CDD and 4CDF to 1 pg/m^3 for 8CDD and 8CDF) were obtained for the field samples. These detection limits are lower than those required if one accepts the New York State Health Department recommendation of an acceptable daily intake of 2 (pg/Kg)/day for 2378-TCDD in humans(5).

A further set of four experimental ambient air collections was carried out as follows:

Sample 1: Filter + Single PUF + High Level Spike (24 hours)

Sample 2: Filter + Single PUF + Low Level Spike (24 hours)

Sample 3: Filter + Dual PUFs + High Level Spike (72 hours)

Sample 4: Filter + Dual PUFs + :pw :eve; Spike)72 hours)

These samples were collected over the period from May 1987 to July 1987. ^{13}C -4CDD, ^{13}C -8CDD, ^{13}C -5CDF and ^{13}C -7CDF were spiked on the filter and ^{13}C -5CDD, ^{13}C -7CDD, ^{13}C -4CDF and ^{13}C -8CDF were spiked on the PUF cartridges of samples 2, 3, and 4. Sample 1 spikes were reversed. ^{13}C -6CDD was used as an extraction efficiency spike. Detection limits of 0.02 pg/m^3 0.05 pg/m^3 for the lower congeners (4CDD & 4CDF) and 0.08 pg/m^3 to 0.7 pg/m^3 for the higher congeners (8CDD & 8CDF) were obtained.

Low recoveries of the tetra- and penta- congeners and higher recoveries of the hexa- to octa- congeners were observed for the filter samples from all four field runs. In sample 1 (Single PUF/High Spike/24 hours collection) 50-100% recovery of the congeners spiked on the PUF was obtained. There was higher recovery of the hepta- and octa- congeners than of the more volatile tetra- and penta- congeners. The PUFs were also monitored for the congeners that were originally spiked on the filters. High levels for the 4CDF and 5CDD were observed, indicating a high degree of breakthrough from the filter to the PUF. There was a lesser degree of breakthrough from the PUF cartridge.

Lower recovery of PUF spikes were obtained for sample 2 (Single PUF/Low Spike/24hr collection). ^{13}C -8CDF was not observed on the PUF at the low spike levels used. Breakthrough of the labelled congeners from the filters onto the PUFs was also observed.

One conclusion that can be drawn from the results for the single PUF experiments is that the MOE sampler allows the determination of ambient dioxins and furans in both the particulate state and vapour phase. It can also be concluded that a single PUF cartridge may be adequate for ambient air monitoring as there is no significant breakthrough from the cartridge. The lower recoveries obtained in sample 2 for the labelled congeners were not a breakthrough problem but a detection limit problem. The spike levels used were close to the detection limits and losses in extraction and cleanup could have dropped the levels below the detection limit.

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